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SPECTROSCOPY IN THEORY AND PRACTICE

by

Walter William Holt

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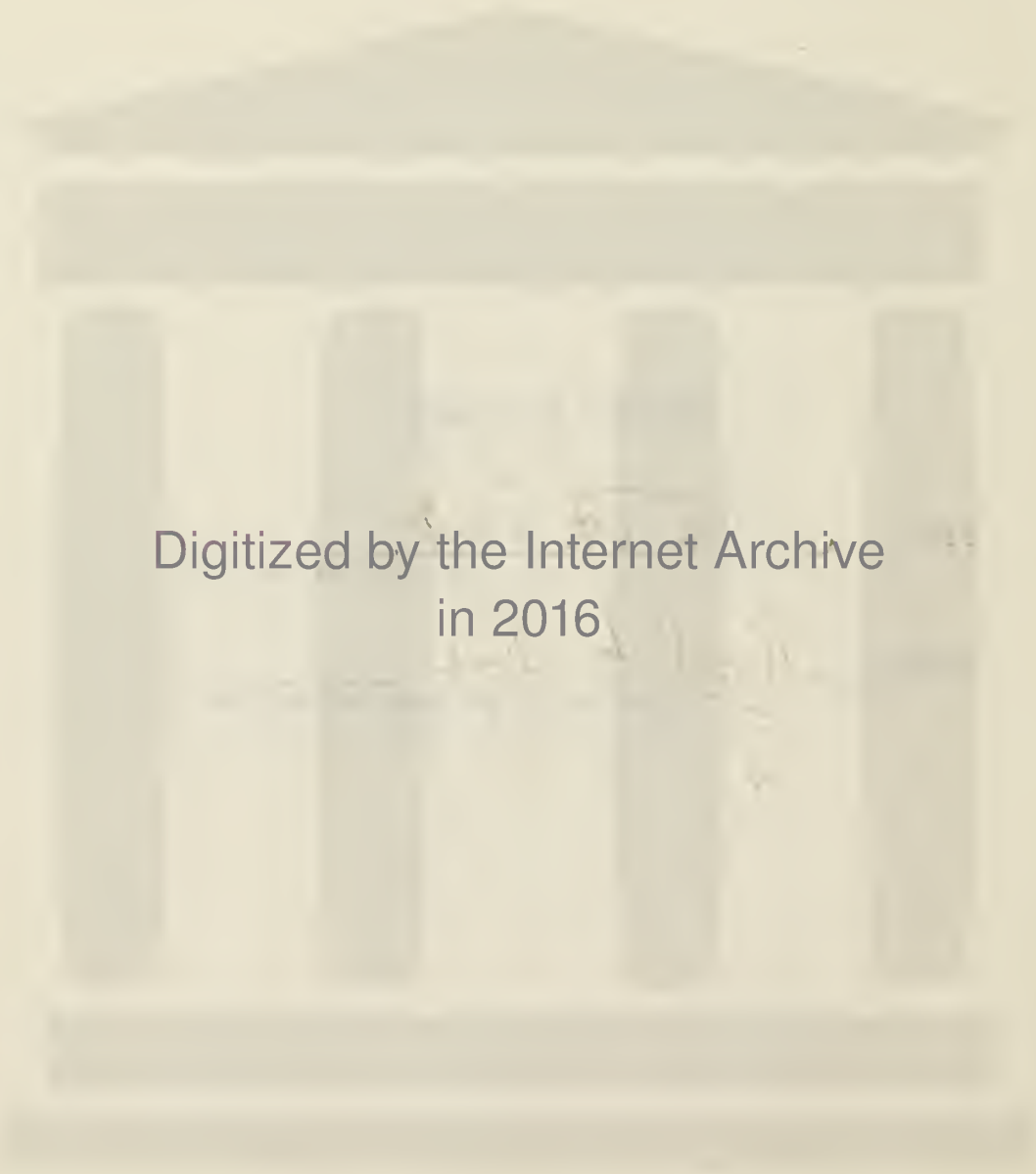
APPROVAL BY READERS

FIRST Norton A. Kent.
Professor of Physics

SECOND Royal M. Fuge
Assistant Professor of Physics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SPECTROSCOPY IN THEORY AND PRACTICE

Introduction

Today, the spectroscope is considered by leading scientists to be the most wonderful single instrument in the field of scientific endeavor and research. Without a doubt, this instrument has taken the place of the microscope in number one position, even though the latter is still making great strides. The spectroscope is far ahead in its revelations of nature's secrets and laws. One has only to delve into its findings to be amazed at its possibilities. In this paper we hope to show the development of spectroscopy along with the theory and practice of the more important instruments, such as, prism spectroscopes, gratings, echelons, interferometers, and the Lummer-Gehrcke Plate.

With one type of this instrument in the laboratory one may analyze the residue of the purest drinking water, although the residue weighs but the 3000th part of a grain, determining accurately the portions in which sodium, calcium, magnesium, and many other elements are present. Or one may direct the spectroscope at the sun or some distant star to determine its composition, shape, size, and speed with which it is moving,either toward or away from the earth. The modern quartz spectroscope will reveal qualitatively and quantitatively the major elements in steel to such small amounts as one part in a million which is

not only many times more sensitive than any other known laboratory method but is the only one possible today by which very minute amounts of matter can be detected. Many of our elements have been discovered by its use. The light given out by a candle may be compared with that emitted by an electric arc, both in quality and quantity. One could continue to present the marvels of the spectroscope, but in this paper it will suffice to add only one more of its triumphs, that is, the measurement of the wave-length of light by the most accurate methods known to science. Visible units of length can be measured most accurately by it in terms of wave-lengths and many countries have adopted the spectroscopic meter as the standard of length.

Historical

The origin of the science of spectroscopy may be traced back to the year of 1666, when Sir Isaac Newton discovered that the rays of different colors underwent different degrees of refraction by a glass prism. He also discovered that a ray of light from the sun was composed of a combination of different colors which suffered different amounts of refraction or bending on being made to pass through a glass prism. The violet ray was bent most and the red least. These colors coming from the prism and forming a series of images on a screen were called a spectrum. Newton even improved the quality of the spectrum by putting a lens between the source of light and the prism. In 1801, Wollaston improved the manner of the experiment by employing a ray

of sunlight passing through a narrow slit, which functioned as a source of light in one dimension, and observed that the spectrum was crossed by a number of black lines parallel to the slit. A few years later in 1814, Fraunhofer, the celebrated optician at Munich, studied these lines very carefully and thoroughly.

First, however, he greatly improved the apparatus for studying the spectrum by placing a convex lens between the slit and the prism, and eventually applied a telescope for viewing the spectrum. In short, he invented the best known of the many forms of the spectroscope with which we are familiar today and really laid the foundations of the modern science of spectroscopy. In studying these dark lines from the solar spectrum, Fraunhofer recognized that their relations to one another were constant, and mapped the position of approximately seven hundred of them. The principal ones he designated by letters A to H, A being in the red and H in the violet. While he as well as other men of science did not understand the phenomenon of the black lines, he did realize that sometime that they would be important as landmarks in the measurement of the refrangibility of the different colored rays.

Later on he followed up the work of Thomas Young, who in 1801 gave forth to the world the principle of interference, and constructed for himself gratings with which he measured the

wave-lengths of the D lines to a remarkable degree of accuracy. His first gratings were made by winding silver wire around a brass frame so that the grating spaces were quite equal. Then he succeeded in making gratings by ruling equidistant and parallel straight lines on flat glass plates with grating spaces equal to .0033 mm. and .016 mm. respectively. With these glass gratings he found the wave-length of the D line to be 5886 A.U. and 5890 A.U. respectively. The importance of his work cannot be overestimated for he first showed by his work on the black lines of the solar spectrum, which bear his name, the possibility of making accurate measurements of the relative dispersive powers of substances, and his ingenuity in making a grating founded an absolute method of measuring wave-lengths of light.

While the actual significance of the black lines in the spectrum of sunlight was unknown to Fraunhofer, years passed before the whole matter was investigated and completely explained by Kirchhoff in 1859. He not only gave mathematical deductions but experimental proof of the great law which bears his name. "The ratio between the powers of emission and the powers of absorption for rays of the same wave-length is constant for all bodies at the same temperature." Not only did his explanation give much information as to the actual composition of the sun, but it gave great impetus to spectroscopic work. Of all those associated with this work, Bunsen and Kirchhoff did outstanding work. They succeeded in obtaining reversals of a

number of lines in the laboratory, thus establishing the presence of many elements in the sun.

Since Bunsen and Kirchhoff proved the existence of many earthly elements in the sun it was a natural sequence that the solar spectrum should come to be the standard of reference. Following in the footsteps of Bunsen and Kirchhoff, A. J. Ångstrom measured and mapped the solar spectrum which he published in 1868 under the name of the Normal Solar Spectrum. This momentous piece of work covered the region between A and H which comprises the visible spectrum. His unit of wave-length was one ten millionth of a millimeter and today it is called an Ångstrom Unit (or just A.U.) in his honor.

The publication of Ångstrom's map marked another important period in spectroscopy for it was the first time that a standard of reference was to be had for all workers in this field of work. Determination of wave-lengths of lines in unknown spectra was made possible by a direct comparison between the unknown spectra and the sun, and the calculation of the unknown wave-lengths by a single process of interpolation between those lines in Ångstrom's map. It, also, stimulated different investigators to compare their results with its data and to compare their results with each other.

While work was proceeding on the visible spectrum, which consists of wave-lengths from 7600 to 3900 A.U., work had been done on the measurement of wave-lengths between the limits

3,140,000 and 1030 A.U. The first one to point out the invisible region beyond the violet was the celebrated chemist Scheele in 1777. He found that the ultra-violet rays caused silver chloride, a white salt, to turn to a purplish color. Yet the actual discoverer of the invisible spectrum was Sir William Herschel in 1800. He caused a beam of sunlight to pass through a prism and tested all colors as to the heating effect on the bulb of a very sensitive thermometer, and found that the region beyond the red had a maximum effect. Later on Sir John Herschel continued the investigation far beyond the visible spectrum. Other important workers in this region were Langley, Paschen, and Rubens.

Ångstrom's solar map was superseded by the publication of Roland's Complete Normal Photographic Map of the Solar Spectrum, based on a new investigation coupled with better gratings and a new type of mounting. This map was about 20 meters long and had a scale of wave-lengths attached. In general, with a new determination of the D lines, his results were greater than those on Ångstrom's map and were considered quite accurate. Later on in 1894, Michelson, by a new method, i.e., by an interference apparatus, succeeded in determining the absolute wave-lengths of three lines in the spectrum of cadmium in relation to the standard meter at Paris. The actual values were:

Red line	1 meter = 1553163.5x λ	λ = 6438.4722 A.U.
Green "	" " = 1900249.7x λ	λ = 5085.8240 "
Blue "	" " = 2083372.1x λ	λ = 4799.9107 "

And so, grating measurements gave place to interference measurements for the greatest accuracy. It was decided at the International Union for Solar Research, held at Meudon in 1907, that the red line of cadmium should be the primary standard and its wave-length was taken as 6438.4696 A.U. In 1908 Fabry and Buisson published a series of measurements of lines in the arc spectrum of iron to serve as secondary standards. And still later, Kayser published a long list of tertiary standards of the iron arc, i.e., lines determined by interpolation between secondary standards.

Spectra

Before taking up a description and theory of the various important instruments of spectroscopy in this paper it will be advisible to discuss briefly various kinds of spectra. They may be divided into two classes: (1) Emission Spectra and (2) Absorption Spectra. Emission spectra are those that result from the breaking up or dispersion of light emitted by a luminous substance under examination, while an absorption spectrum results when light rays pass through a medium which absorbs, extinguishes, or reduces their intensity before they enter the slit of the spectroscope.

One method of classifying emission spectra is by their general character: (1) continuous spectra, (2) banded spectra, and (3) line spectra. The first shows a continuous sequence of colors changing gradually from red to yellow to blue to violet

and a little beyond into the ultra-violet region. It is produced by incandescent solids and can readily be shown by an acetylene flame. The second one gives fluted strips or bands in its formation which occur when a compound is heated to incandescence and is in the undissociated state. It also can be resolved into groups of very fine lines. And the last, the line spectrum, consists of more or less sharply defined lines which are generally distributed without any apparent regularity. They result from electronic disturbances. Lines may be described as "principle", "diffuse", "sharp", etc., which are very significant to the trained investigator. In short, while the two former types of spectra have their place in spectroscopy, the line spectra are the most important in the identification of the elements under consideration.

Another method of classification of emission spectra is by the method of excitation which may be grouped as follows: (1) Flame spectra, (2) Arc spectra, and (3) Spark spectra.

The flame spectrum, perhaps, is most conveniently produced by means of a Bunsen flame for restricted use with a few elements. Since a non-luminous flame gives only a feeble spectrum, any materials introduced into it give their spectral lines. The temperature, about 1700^{o}C is suffiently high to volatilize the salts introduced into it so as to give their characteristic spectra. For example, a platinum wire, first having been completely cleansed with HCl is dipped into a NaCl solution and is then introduced into the Bunsen flame which latter becomes

yellow. On examining the light by the spectroscope the spectrum is found to consist of many doublets, those especially strong being a pair in the yellow. The metals which give flame colorations easily are sodium, potassium, rubidium, caesium, barium, strontium, and calcium; also, indium, gallium, and thallium. Anyone working with the salts of the above mentioned metals on a platinum wire will readily see that they quickly burn off showing that this method is generally limited to work with a visible spectroscope. Other types of flames have been used with success and other complicated methods of causing the materials to burn a long time have been used, but a description of these methods is beyond the scope of this paper.

Arc spectra form a second method of producing illumination, discovered by Sir Humphrey Davy in 1802, but not freely used for spectroscopic work until the dawn of the present century when electricity was generated by the dynamo. Their value depends on the exceedingly high temperature of the arc-- in the neighborhood of 4000°C-- considerably hotter than any flame. Consequently, many more elements may be examined by this method than by the flame. This method is easy to handle and the materials in the solid state may be used with little preparation. The electrodes can either be made of the materials under consideration or the materials may be put in a core of a positive carbon electrode. After the current is flowing freely the electrodes are put about 1 mm apart. The light coming from the arc is focused on the slit of a spectroscope by a lens. Upon

examination it is found that the spectrum of the arc is continuous while that of the vapor consists of a mass of fine lines.

Electric spark spectra, as the term indicates, are produced when an induction coil is used. Here, generally, a very heavy spark is desirable to get good results. The intensity of the spark is increased by placing a number of condensers, usually Leyden jars, in parallel with the spark gap. In general, the electric spark produces two spectra, first, the spectra of the electrodes and secondly, the spectrum of the air or other gases between the electrodes. Solids and alloys are often examined by this method; also various gases, by enclosing them in tubes under low pressure carrying platinum electrodes at each end.

ABSORPTION SPECTRA. While the absorption spectrum of the sun showing Fraunhofer lines is most familiar to all, this type of spectrum may be produced in the laboratory in various ways. If one should place a non-opaque substance between the source emitting a continuous range of wave-lengths and the slit of a spectroscope, some wave-lengths are found to be absorbed corresponding to the dark places on the spectrum. For example, if one uses a red glass as the absorbing medium, only red light is transmitted. In the case where gases act as the absorbing medium, sharp dark lines may be obtained in place of the emission spectrum.

LINES OF ELEMENTS. The spectral lines of all elements under consideration are characteristic of their element in that they are always the same if conditions are maintained the same. While different types of excitation bring forth more strongly the various lines, a line with the wave-length 4226.73 A.U. indicates that calcium is present. And so it is with every other element. Some elements give only a relatively small number of lines while others emit thousands which are easily recognized by the trained investigator. Furthermore, these spectral lines are narrow images of the slit caused by the different wave-lengths of light emitted by the source.

DETERMINATION OF WAVE-LENGTH. There are two general methods by which wave-lengths may be determined (a) the visible spectrum (b) the photographed spectrum. With the first method there are two ways. First, by using an instrument fitted with a drum-index graduated to read directly in wave-lengths the lines under consideration; and second, by means of an arbitrary scale, such as the vernier on the table of the spectrometer. The second or spectrogram method gives much better results than the first for various reasons. Quite often the spectrum of a substance is photographed upon a plate in juxtaposition with a scale of known wave-lengths. Then by means of a travelling microscope or an instrument known as a comparator, the wave-lengths of the lines can be measured. Today, the determination of the wave-length of the line may be done by hand or auto-

matically by a photo-electric cell. By comparing the wave-lengths of the spectral lines with wave-length tables, identification of the element or elements under consideration can be made.

PLATE I

The Bunsen Spectroscope

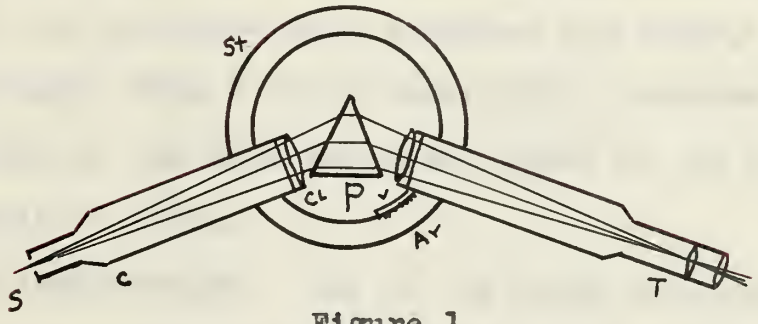

Figure 1

Formation of the Spectrum

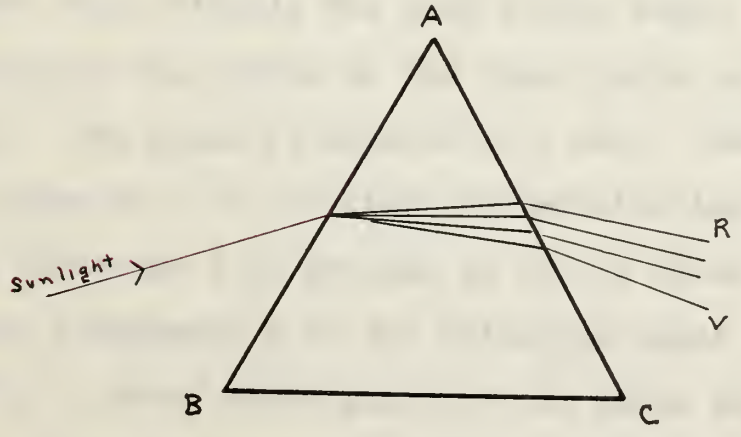

Figure 2

THE PRISM SPECTROSCOPE

In considering the apparatus for the analysis and measurement of various spectra, the prism spectroscope will first be considered, together with its essential accessories. A description of the apparatus with diagrams and theory will suffice to show its use. Then a brief description together with the theory and use of the more important kinds of the prism spectroscopes will be given.

BUNSEN SPECTROSCOPE. One of the usual arrangements for an ordinary Bunsen spectroscope is shown diagrammatically in figure 1, plate I. The light to be examined is generally passed through a lens to focus the light on slit S which restricts the source to a very narrow line. The collimating lens CL causes the beam of light to be parallel before it falls on the prism P, which not only refracts but also brings about its dispersion. The telescope then picks up the light which is viewed by the observer. The prism is mounted on a small table in the center of the stage St. To the stage the collimating tube C is fixed and the telescope T is movable in an arc at Ar on the other side. A vernier attachment V on the telescope makes the readings more accurate. A brief description of the parts will make the working of the spectroscope understandable.

THE SLIT. The slit is generally very narrow, with its sides straight, parallel, smooth, bevelled inwardly, and clean. Usually the slit is adjustable by a very fine screw, both jaws

being movable in the better instruments and only one in the cheaper. When the slit is about one hundreth of a mm. apart good spectra are generally obtained. The height of the slit should be just tall enough to fill the collimator lens with light.

THE COLLIMATOR. The collimator consists of a metal tube carrying the slit at one end and a converging lens at the other. The focus of the lens is at the slit, therefore, all the rays leaving the lens will be parallel when they fall upon the face of the prism, which arrangement gives a well defined spectrum.

THE PRISM. The prism is the main unit as it produces the spectrum. Generally, in the ordinary spectroscope for visible work, it is made of glass.

THE TELESCOPE. The function of the telescope is to collect all rays from the slit and focus them on the eye of the observer. It can be moved about on its arc to focus on any particular part of the spectrum desired. The lenses used in the telescope and collimator are usually made up by cementing two different kinds of glass together to prevent chromatic aberration. Sometimes a third tube (not shown in diagram) is attached to the stage with a lighted scale from which wavelengths can be read directly while viewing the different spectral lines.

THEORY OF THE PRISM. When a beam of sunlight passes through a prism, it is bent through a certain angle from the

PLATE II

Deviation in a Prism

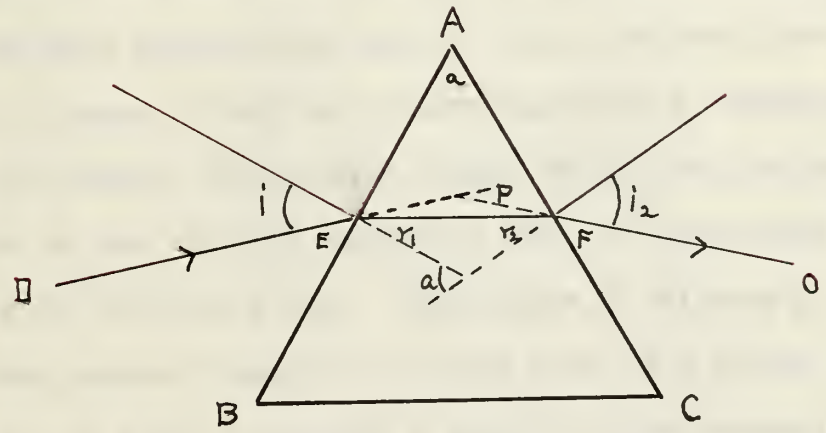

Figure 3

A Direct Vision Spectroscope

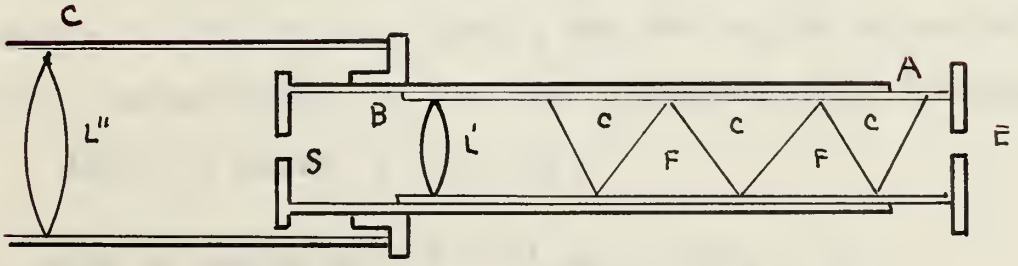

Figure 4

direction in which it was originally travelling. This bending arises from the fact that the velocity of light in air is different from that in the material of which the prism is made. Since most sources treat light of different colors, the rays will be bent differently due to the fact that their velocities differ. Hence a band of colors known as a spectrum will emerge from the prism. The violet light which has the shortest wavelengths in the visible spectrum will be bent most while red light will be bent least. See Plate I, Figure 2.

The general theory of refraction in a prism is best understood if we first consider a beam of monochromatic light as our source of light. In Plate II, figure 3, an incident beam of light DE strikes the side of AB where it is refracted, taking the course EF, and finally is refracted again at the face AC in the direction FO. The angle P, between the incident and emergent rays is called the angle of deviation. Calling the angles of incidence i_1 and r_2 and the angles of refraction r_1 and i_2 respectively, we find the following relationships:

$$\text{Angle of prism} = a = r_1 + r_2$$

and $$\text{Angle of deviation} = P = (i_1 - r_1) + (i_2 - r_2)$$
$$= (i_1 + i_2) - a$$

The two above equations depend upon the fact that the exterior angle of a triangle is equal to the sum of the two opposite interior angles. With these two equations we can readily compute the deviation of a ray if we know the values of i_1, i_2,

r_1, r_2, and a.

In order to determine the index of refraction μ, of a prism, it is generally best to set the prism at minimum deviation, i.e. so that i_1 equals i_2, and the ray within the prism is perfectly symmetrical with reference to the refracting faces. This position is of great usefulness in ordinary spectroscopic work. By substituting equivalent values for i and r in

Snell's Law $$\mu = \frac{\sin i}{\sin r}$$

We have $$\mu = \frac{\sin\left(\frac{a + P}{2}\right)}{\sin\left(\frac{a}{2}\right)}$$

The value of $\underline{a}$ or angle BAC can readily be determined by measuring the angle between the rays reflected from the two refracting faces. This can be done by various methods, but, perhaps the simplest one is by using the spectrometer. The collimator is arranged so as to send the light toward the edge A of the prism (with the ray perpendicular to BC). The telescope is trained upon the image of the slit as reflected from the face AC of the prism and the angle noted. Then the telescope is turned and adjusted to the reflected image from the face AB of the prism. The position is again read, and the difference between the two readings will be just twice the angle A.

The value of i can be determined by first placing the face

AB of the prism perpendicular to the source of light and noting the number of degrees on the table. Then by rotating the prism until minimum deviation is obtained with monochromatic light, the difference in the two readings will give the value of i or the angle of incidence.

DISPERSION OF A PRISM. Briefly, we may say that the dispersion of a medium is given by the expression $\frac{d\theta}{d\lambda}$. We may illustrate with the two sodium lines. The wave-lengths of D_1 and D_2 are 5896 A and 5890 A respectively. If we divide the difference in the angles of emergence (or $d\theta$) of the light from the prism forming these two lines by the difference of wave-length $d\lambda$, we have the dispersion.

RESOLVING POWER OF A PRISM. The value of a spectroscope often depends upon its resolving power and the brightness of the spectra it produces. The brightness of the spectra depends on the aperture of the instrument along with the size and kind of material of which the prism is made. Usually to get the best results the width of the beam of light should just fill the prism. While a large part of the light passes through the prism, some of it is reflected on the first face and some of it is absorbed by the prism itself. These losses lessen the brightness of the spectra proportionately. Again, in the case of the two sodium lines, let λ and $(\lambda + d\lambda)$ equal the wave-lengths of the two D lines. If when the slit is narrow enough we see the two lines just separated in the telescope, then

$\frac{\lambda}{d\lambda}$ is said to be the resolving power of the prism for that part of the spectrum. The formula

$$\frac{\lambda}{d\lambda} \quad t\frac{d\mu}{d\lambda}$$

is the resolving power of a prism spectroscope where t equals the base of the prism, μ is the index of refraction of the prism, and λ the wave-length of the light. The resolving power of prisms thus varies with the materials out of which they are made. For example, the resolving power of a flint glass prism is much greater than one made of crown glass.

PRISM MATERIALS. The ordinary materials out of which prisms are made are as follows: carbon disulphide, glass, quartz, calcite, fluorite, sylvin, and rocksalt. Glass prisms are most commonly used in the visible region for they are plentiful, cheap, and have a great range of dispersive power. Quartz, calcite, and fluorite are used in the ultra-violet for they are transparent to short wave-lengths, while rocksalt and sylvin are used in the infra-red where the wave-lengths are long.

THE DIRECT VISION PRISM SPECTROSCOPE. The direct vision spectroscope as shown diagrammatically in plate II, figure 4, is one of the simplest and most practical of all spectroscopes. This instrument consists of two tubes, A and B, which slide one into the other. The larger tube B, carries the slit, S, and t the smaller tube A carries the prism train and the lens L'. The

PLATE III

A Constant Deviation Prism

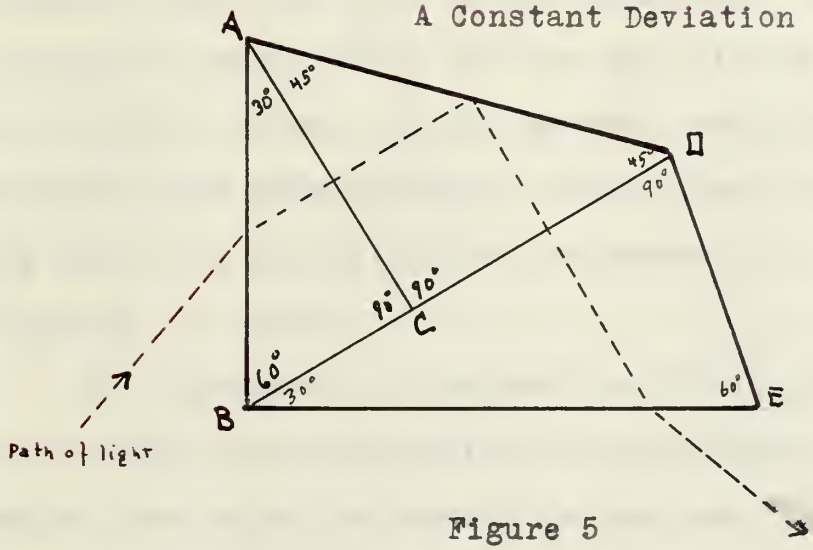

Figure 5

The Littrow Spectroscope Arrangement

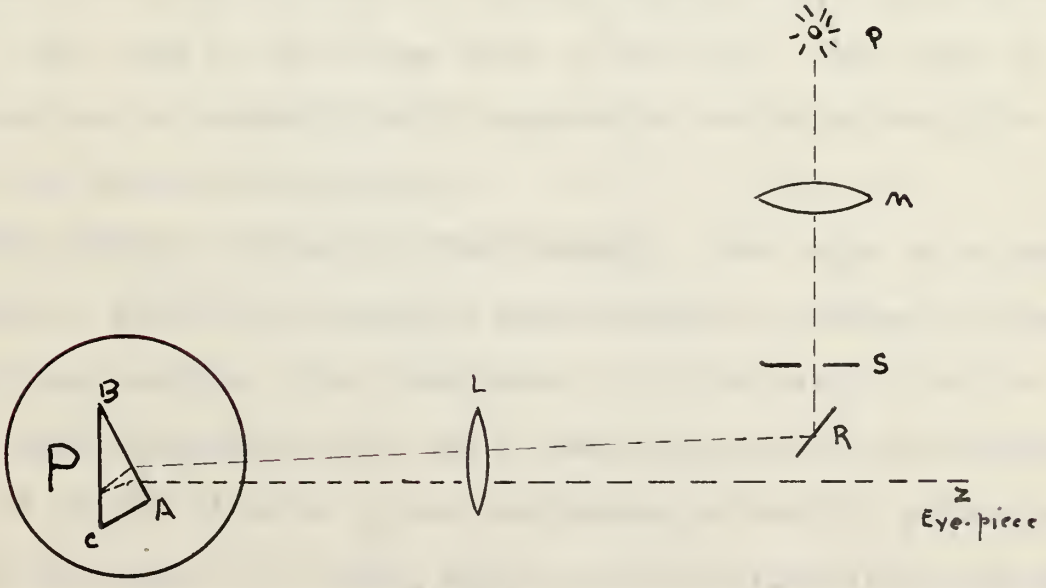

Figure 6

slit consists of an aperture of definite or variable width depending upon the cost of the apparatus. The lens L' is an achromat of short focus and the prism train generally consists of two flint prisms and the three crown-glass prisms cemented together with Canada balsam. This prism train is packed into the tube with strips of cork to prevent its slipping. At E a diaphragm is fitted.

The instrument is focussed by sliding the smaller tube in or out until the best definition is secured. L" is a collimating lens which is mounted in the tube C which can slide over tube B in order to focus the rays upon the the slit. There is no telescope as the eye comes up close to the prism. Usually there is no way to measure the wave-length of any line, but sometimes this can be done by a scale which is seen by reflection in the side of the prism next to the eye. This type of a spectroscope is comparatively inexpensive and very handy for rough work in the laboratory.

THE CONSTANT DEVIATION SPECTROSCOPE. This type of a spectroscope is used where accuracy and automatic readings of observations are desired. The instrument is fitted with a collimating tube carrying a slit and a condensing lens. The prism consists of one piece of glass equivalent to two 30° prisms set against the faces of a right angle totally reflecting prism and has the property of always giving the same deviation, 90° for any ray under investigation at the center of the field. The

constant-deviation prism as represented in plate III, figure 5, consists of prism ABC, of which the angles are ABC = 60°, BAC = 30°, and ACB = 90°, ACD = 90°, CAD = 45°, and ADC = 45°.

When a ray of light enters the prism ABC at minimum deviation, making an angle of incidence i at the surface AB, it travels through the prism parallel to the base BC and enters prism ACD at normal incidence, hence it suffers no refraction. The ray is then totally reflected at surface AD and enters prism BDE at normal incidence, travelling parallel to the base DE, and finally emerges from the face BE, making angle e with the normal. As angles i and e are equal since the light traverses both 30° prisms at minimum deviation, and as the faces AB and BE are at right angles to each other, it follows that when a ray of light passes through this prism it is deviated 90°.

In practice, it is simply necessary to fix the collimator and telescope permanently at right angles to each other. Then by rotation of the prism around a vertical axis the different portions of the spectrum can be brought into view at minimum deviation. This prism is cut from a single piece of glass in such a way that the four vertical faces enclose four angles equal to the combination of the three imaginary prisms cemented together. In order to bring the rays of successive wave-lengths into view, the prism is mounted upon a table which is turned by pressure from a screw against a small arm. This screw is the

spindle of a drum whose wall is pierced with a helical groove from which the wave-lengths of the ray may be read directly.

THE OBJECTIVE PRISM SPECTROSCOPE. The objective prism or slitless spectroscope consists of a large prism, usually with a rather small angle placed in front of the objective of a photographic telescope. No slit is needed since the star is the point source, and no collimator, since the rays are parallel. The spectra appear as narrow streaks on a plate placed in the focal plane of the telescope. In photographing with an objective prism the spectra are given the necessary width for examination by slightly changing the rate of the driving clock so that there is a slight and gradual drift in the right ascension. Since the refracting edge of the prism is being turned parallel to the diurnal motion of this drift, this drift gradually widens the spectrum to the extent of a few minutes of arc during the whole exposure. The advantages of this type of instrument are that there is little loss of light and many spectra may be photographed at once, as all the stars in the field of the instrument leave their images spread out into a spectrum upon the photographic plate. Best results are obtained by using a portrait camera in photographing lines. If the light is bright enough to warrant high dispersion, several prisms in tandem may be used.

THE LITTROW PRISM SPECTROSCOPE. In the Littrow instrument only one half-prism is used, but it functions as a whole prism

in that the ray is refracted by it twice, first in the ordinary way as far as face BC in plate III, figure 6, and then because it is silvered to form a mirror, it is reflected back and at AB is further dispersed. Light from the source Q is focused by lens M on the slit S, reflected at R and passes through the lens L to half-prism P. The spectrum so formed is viewed at point Z, either by an eye-piece or a photographic plate. The system of using the same tube for the passage of light in both directions is known as "auto-collimation".

The prism table with the prism is rotated by means of a tangent screw carrying a drum-head, upon which is a scroll graduated in wave-lengths. The eye-piece carries a spider-web which can be set upon the spectrum line, and the wave-length can be read directly from the drum-head. Since it is possible to view or photograph the three regions of the spectrum separately, it is of great advantage when studying complex spectra, such as those of iron, tungsten, the rare earths, etc.

PLATE IV

Section of a Diffraction Grating

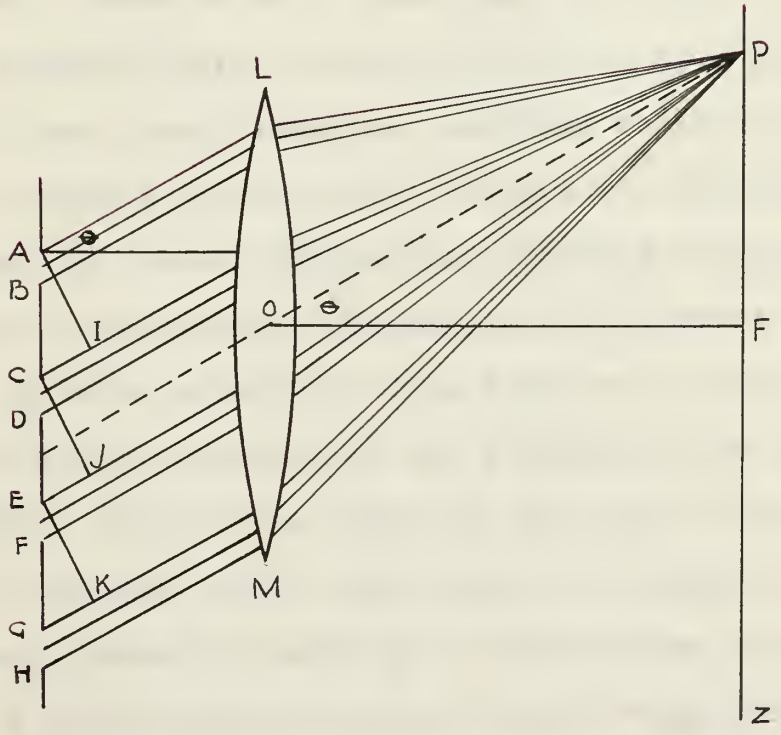

Figure 7

DIFFRACTION GRATING SPECTROSCOPES

Another very important class of spectroscopes is of the grating type. Gratings usually consist of a number of fine, equidistant, and parallel lines ruled on glass or speculum metal, or of casts made from a metal grating. The latter are known as replicas. As has already been mentioned in this paper the first gratings were made by winding silver wire uniformly and equidistantly about a brass holder. Then they were made on plane glass. Later speculum metal was used for it is much softer and easier to work than glass. Replicas are used where absolute accuracy is not needed for they cost but a small fraction of what a good grating costs. Diffraction gratings can be divided into two classes: transmission gratings and reflection gratings. The first include wire gratings, those ruled on glass, and replicas. And the second consists of all gratings ruled on metal.

DIFFRACTION. Grimaldi in 1665 was the first to notice that a beam of light passing by the sharp edge of an opaque object suffers a certain amount of bending or diffraction as he called it. Some years later Thomas Young and Fresnel explained the reason for this phenomenon by the application of the wave theory of light. This theory that light consisted of transverse waves was first developed by Huyghens. He put forth the idea that when light travels through space consisting of ether particles each ether particle becomes the source of a new system of vibrations. Every particle in the front surface of a wave-front

becomes the source of a new system of waves, and the resulting disturbances form a new wave-front. In accordance with this theory we find that when rays of light from different grating spaces are in phase, or one or more whole wave-lengths apart we have a maximum of light. And when the wave-lengths of the rays from the grating spaces are any number of odd half-wave-lengths apart, they destroy each other, or we have interference, resulting in a minimum or darkness.

DIFFRACTION GRATING. In the case of glass transmission gratings where the diamond point has made a furrow, light cannot go through it, at least, not regularly as it does between the rulings. We might liken the rulings to an old fashioned picket fence. They differ in one respect, however, in that the pickets are far apart while the rulings are very close together, sometimes as many as 10,000 or 20,000 of them to the inch.

Let AH in plate IV, figure 7, represent a section of such a grating on which is falling parallel light so that the direction of light is perpendicular to the plane of the grating. Through the slits in the glass will come the beams of parallel monochromatic light. These beams will be brought to a focus in a bright line on the screen PZ, by the lens LM, at the point F. If the light is viewed in a direction making an angle θ with the normal OF, to the grating, parallel rays of light emerging from the slits in this direction will travel unequal distances to reach the screen, and when they are brought to a focus at P

by the lens LM, they may either reinforce or destroy each other. If the angle θ is made such that a ray of light from one slit is one-half a wave-length behind the ray of light from the preceding slit, then the rays from one slit will be out of phase with the neighboring ones and will destroy each other, resulting in darkness or what is known in spectroscopic language as a minimum.

If the angle θ is gradually made larger, the rays from the lower slits will be more and more behind the rays of the upper slits. When the rays of two neighboring slits are just one wave-length apart, i.e., when the wave-length of rays through slit CD are just one wave-length behind the wave-length of rays passing through slit AB, reinforcement occurs and a bright line is produced at P which is called a maximum. The first bright line from the point P is called the maximum of the first order, and all succeeding ones are numbered in their numerical order. By moving the lens or the telescope gradually in one direction, alternate maximum and minimum will be seen.

Let us now consider the geometry of the figure 7. If θ_1 is the angular distance from F of the first bright maximum, θ_2 of the second, or generally θ_n, of the nth, and since the triangles POF, ACI, CEJ, and EGK are similar, we have

$$\angle POF = \angle CAI = \angle ECJ = \angle GEK$$

Hence $CI = AC \sin \theta$

When $CI = AC \sin \theta = \frac{\lambda}{2}$

PLATE V

Incident Rays Not Perpendicular to the Grating

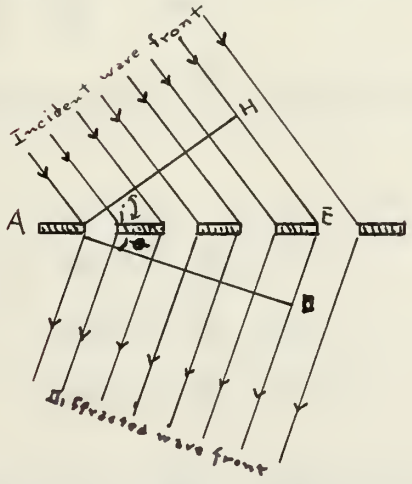

Figure 8

The Reflection Grating

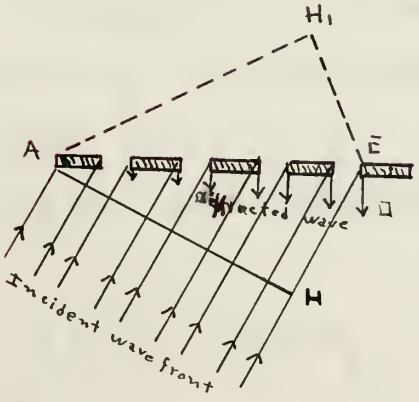

Figure 9

$$\text{or} \quad = AC \sin \theta = \frac{3\lambda}{2}$$

$$\text{or} \quad = AC \sin 0 = \frac{5\lambda}{2} \quad \text{etc.}$$

the rays from the different slits destroy each other, and we have minima.

$$\text{When} \quad CI = AC \sin \theta_1 = \lambda$$

$$\text{or} \quad = AC \sin \theta_2 = 2\lambda$$

$$\text{or generally} \quad = AC \sin \theta_n = n\lambda$$

the rays from the different slits reinforce each other and we have maxima.

The angle θ through which the telescope of the spectrometer must be turned before reinforcement is again obtained from point F can be measured on the divided circle of the spectrometer. The number of rulings per centimeter of the grating is given by the maker or can be found readily by a high-power travelling microscope. If we let $a + b$ equal the grating element, we find for the first reinforcement of light that we have

$$\lambda = (a + b)\sin \theta_1$$

$$\text{or generally} \quad n\lambda = (a + b)\sin \theta_n$$

Since all quantities in these equations are known except λ, the wave-length of light, can be calculated. By means of a good grating very accurate results for the wave-length may be obtained

If the angle of incidence of the light from the collimator is not zero as shown in plate V, figure 8, but some definite angle, such as i, or angle HAE, then the retardation of the extreme ray, between the two wave fronts AH and AD, is HE + ED. This leads us to the general conclusion that the line at p is bright if the following equation holds:

$$(a + b)(\sin \theta + \sin i) = n \lambda$$

Monochromatic light falling on such a grating will give bright lines on either side of the central image of any order. And when angle i-angle θ = o, we have a condition which is known as minimum deviation for the grating.

So far, we have considered incident rays of monochromatic light falling on the face of the grating. If white light or sunlight falls on the grating the spectrum is produced as it was in the case of the prism. Each color of the composite light gives its own image of the slit. The first order images form two first orders, the second order images form two second order images, etc. The different spectra overlap somewhat. For example, the red of the second order spectrum is superimposed on the green of the third order spectrum.

REFLECTION GRATINGS. Good glass gratings are very difficult to rule for the diamond point used in ruling them deteriorates very rapidly. An alloy metal, known as speculum metal is used for its surface takes on a very high polish and,

since it is not very hard, a diamond point can rule many more lines on it than it can on glass. Speculum metal is generally made up of 32 parts copper, 15 parts of tin, and a small amount of arsenic. A grating ruled on this forms spectra in much the same manner as the glass transmission grating. See plate V, figure 9. The effect is the same as if the incident wave AH were replaced by its image AH, and the grating were at the same time made transparent. In either case the retardation of the extreme ray is HE + DE (see plate V, figure 8) and the position of the spectrum of the nth order is given by the following equation:

$$(a + b)(\sin i + \sin \theta) = n \lambda$$

where i = angle EAH, a + b = the grating element, θ = angle EAD.

GRATING DISPERSION. By definition the dispersion is

$$\frac{d\theta}{d\lambda}$$

as in the case of the prism. Taking the case of the transmission grating for the first order we have

$$\sin \theta_1 = \frac{\lambda}{a + b}$$

By differentiation we have:

$$\frac{d\theta}{d\lambda} = \frac{1}{(a + b)\cos \theta_1}$$

PLATE VI

The Rowland Concave Grating Mount

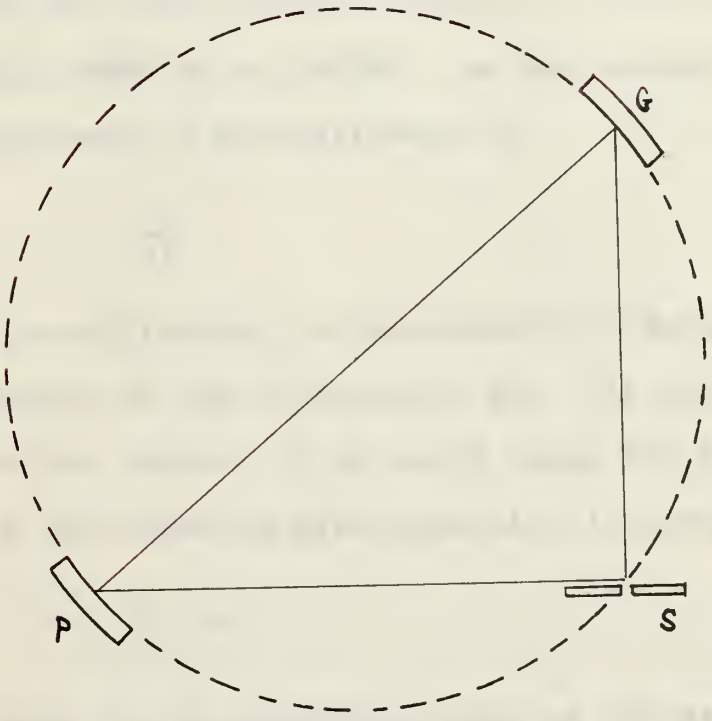

Figure 10

Or generally, for the nth order, we have:

$$\frac{d\theta}{d\lambda} = \frac{n}{(a + b) \cos \theta_n}$$

From the above equation we find that the dispersion increases directly with the order of the spectrum.

RESOLVING POWER OF A GRATING. As has already been stated the resolving power of an instrument is

$$\frac{\lambda}{d\lambda}$$

where $d\lambda$ is the difference in wave-length of two lines that can be just separated by the instrument, and λ is the mean wave-length of the two lines. If we let N equal the number of rulings and n the order we find according to Lord Raleigh that

$$\frac{\lambda}{d\lambda} = Nn = r$$

where r is equal to the resolving power of the instrument.

ROWLAND'S CONCAVE GRATING. Roland's invention of the concave grating was hailed in 1882 as a brilliant optical discovery. It consisted of a grating ruled upon a polished spherically concave surface of speculum metal with the rulings equally spaced on the chord of the arc. All lenses are eliminated in this type of a grating spectroscope. A simple diagrammatic sketch of Roland's concave grating spectroscope is to be found in plate VI, figure 10. The slit S and the grating G are each placed on the circumference of the circle PSG whose diameter is

just equal to the radius of curvature of the grating. The grating may be but a few inches wide while the diameter of the circle may be any number of feet in diameter. Consequently, all spectra will focus on the circumference of the circle and may be seen with an eye-piece or photographed at the point P. This type of a grating is regarded as very convenient to use for all general spectroscopic work and gives extremely sharp spectral lines if conditions are right. Also, its resolving power is very great. In one of his fine gratings which he succeeded in ruling--110,000 lines in a width of 5½ inches, the resolving power for the second order is 220,000. In order to obtain the same result with a flint glass prism in the yellow part of the spectrum it would be necessary for the base of the prism to have a length of about 22 meters.

THE ECHELETTE. Echelette is the name given by R. W. Wood to a type of diffraction grating invented by him which is quite suitable for the measurement of long wave-lengths such as those in the infra-red region. A sheet of copper is half-toned with gold and polished. A carborundum crystal is used for the ruling because its natural edge is so straight that it rules a groove with optically perfect sides. Everything depends upon this fact and the angle at which the crystal is set with respect to the forward and backward motion of the ruling machine. The crystal is so mounted as to rule a groove with one edge at an angle of 20° or less with the original surface. No metal is

removed, the gold is merely compressed under the weight of the crystal in the ruling-machine. With normal incidence, in the case of visible light, this gives us a concentration of energy at an angle of 40°, with practically no energy thrown off from the other edge of the groove, due to the steepness of the angle. Good echelettes show no reflection in the normal direction. Generally there are about 1000 lines to the inch. The dispersion of this type of grating in the region of the long wavelengths is many times that of a prism.

REPLICAS. A copy produced from an opaque grating as a mold, is known as a replica. Lord Raleigh was the first to make replica gratings from ruled gratings by photographic methods. Later better commercial celluloid replicas were made from Rowland gratings simply by letting plastic celluloid harden on the grating to form casts. Thorp was the man who discovered this process. His method was greatly improved upon by R. J. Wallace who used gun-cotton dissolved in amyl acetate in place of the celluloid. He poured the resulting collodion solution over a very clean grating. After allowing the grating to dry slowly for about two hours, he carefully removed the film and mounted it on a piece of plate glass, the latter having been previously coated with a film of hard gelatine. Frederic Ives improved upon this method by removing the films under water and placing them face down on a plane glass. The water was removed by pressure leaving the lines as air spaces between

the glass and films. Then they are sealed up by another glass with a balsom mixture to protect them from injury. Still more recently, Houlevigue has succeeded in coating these transmission grating replicas with a thin metal film electrolytically, thus transforming transmission replicas into reflection replicas, which can be used in the place of concave gratings in a Rowland mount. The big advantage of using these replicas in place of real gratings is their slight cost. The later ones have been so well made that for ordinary laboratory experiments they give very good results.

PLATE VII

The Echelon Grating

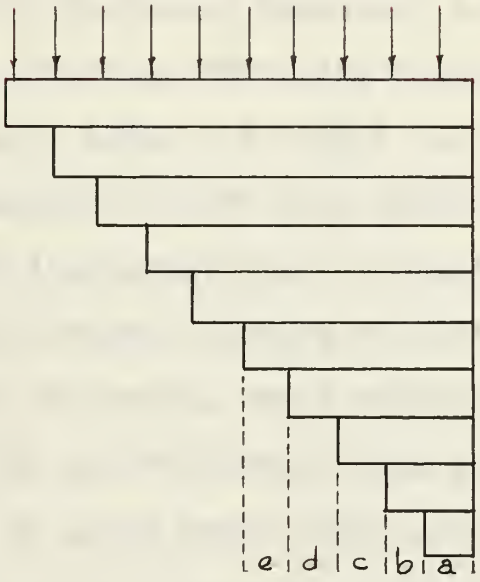

Figure 11

Two Consecutive Steps of an Echelon

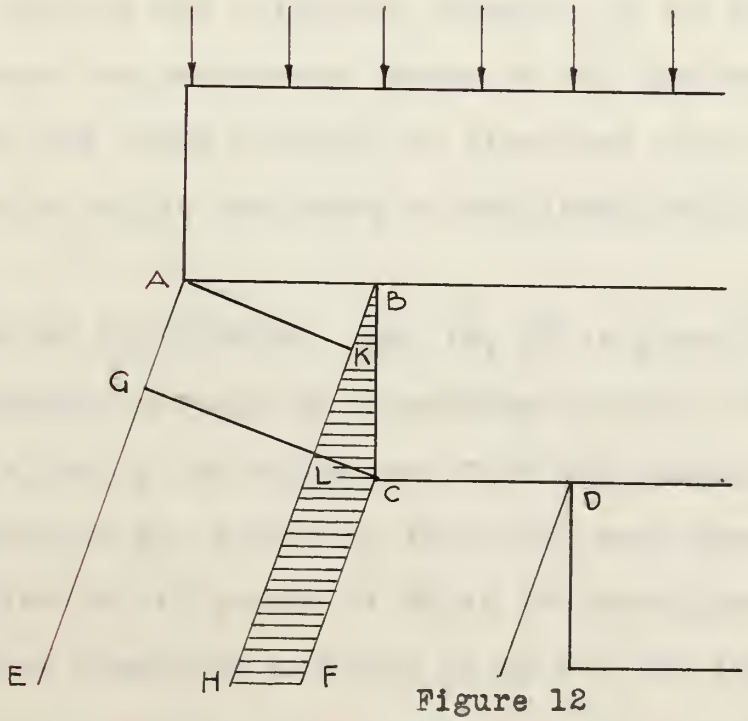

Figure 12

MICHELSON'S ECHELON GRATING

Another important type of spectroscope is the ingenious arrangement designed by Professor Michelson to obtain an enormous increase in the resolving power and brightness of spectra over ordinary gratings. Also, his object was to construct a grating with which spectra of very high orders might be observed. His echelon, as shown diagrammatically in plate VII, figure 11, consisted of setting together a series of perfectly parallel glass plates of equal thickness, which decrease in size by an equal amount. Parallel and uniformly thick plates are generally cut from a slab of glass whose sides are perfectly parallel. The beam of parallel light is incident normally on the top plate in the diagram and the rays after passing through the echelon are brought to a focus by a lens. The rays a, b, c, etc., coming from the different elements of the grating are retarded upon one another by reason of the difference in the velocity of the light through the glass and air; thus interference is set up at the focus of the lens, and a spectrum is formed.

THEORY OF THE ECHELON. Let AB, CD in plate VII, figure 12, be two consecutive steps of an echelon grating. Then let AB = CD = a, while the thickness BC of each plate is equal to t. Light arrives at all points of AB in the same phase and the light arrives at all points of CD in the same phase but this phase differs from that arriving at AB for the light after

passing the plane AB, has to traverse a thickness of glass equal to t before it reaches CD. As usual, let μ be the refractive index of the glass for waves of length λ, which leads us to the conclusion that for these waves, a distance of t in the glass is the same as a distance μt in air.

Now let AE, CF, be parallel rays from corresponding points in steps AB and CD, and draw CG perpendicular to these rays. Draw BH parallel to AE and draw AK perpendicular to BH. Then, if angle CBH equals θ, the diffraction of the ray, AG = KL = BL-BK = BC cos CBL-AB cos ABK = t cos θ -a sin θ. Therefore, we see that the rays AE and CF shall be in the same phase on reaching the plane GC if the differences in the path of these rays, after passing the plave AB are equal to an integral number of wave-lengths. This can be expressed in the following equation:

$$\mu t - (t \cos \theta - a \sin \theta) = n \lambda$$

When the rays AE and CF are in the same phase in the place GC, we find that any two rays parallel to AE and CF, from any corresponding points in the steps AB and CD will be in the same phase in the plane GC. Thus if all the rays from the steps fall on a lens, those that make an angle θ with BC will reinforce each other in the focal plane of the lens. And the above equation will give a condition for a bright line to be formed by the diffracted rays of all the steps of the echelon at an

angle equal to θ.

This instrument can be used to observe orders in the thousands. For example, with an echelon with 30 steps with t equal to 7.8 mm. and a equal to 1 mm., the 8000th order of the D sodium may be examined. And its resolving power is roughly equal to 120,000.

THE ECHELON SPECTROSCOPE. The echelon grating spectroscope generally has a constant deviation spectroscope attached to it for a preliminary analysis of the light going into it. And as usual, a telescope is used to view the spectral lines. This instrument is used mainly for the analysis of monochromatic light for sunlight causes too much overlapping to be practical. Light from a vacuum-tube is first analyzed by a prism spectroscope and one of its lines is thrown on the slit of the echelon spectroscope. The image is then observed by a telescope.

PLATE VIII

The Michelson Interferometer

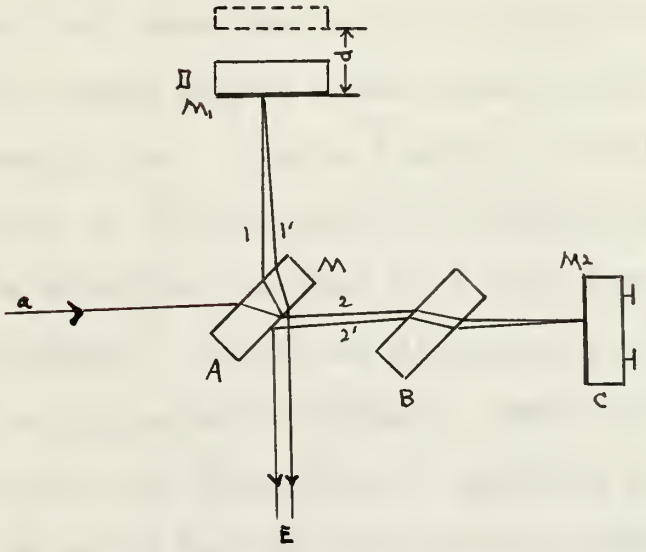

Figure 13

The Fabry and Perot Etalon

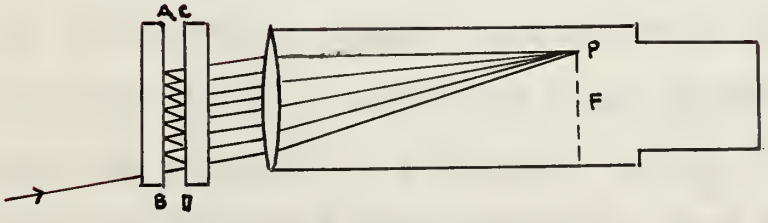

Figure 14

THE INTERFEROMETER

The last important type of the spectroscopes to be discussed in this paper is the interference kind in which a beam of light, coming from a single source, is divided into two portions, which by various means are caused to suffer different amounts of retardation, so that when they are reunited, interference is produced. Professor Michelson was the first to inver such an ingenious instrument. With his apparatus, he was able to study the structure of spectral lines which were so homogeneous as to be beyond the resolving power of any grating, however large. In fact, for the determination of the absolute wave-length of a single line, interferometer methods are the only ones so far known. Another important type of interferometer is that of Fabry and Perot. And still another of importance, while simple in design, is the Lummer-Gehrcke plate.

THE MICHELSON INTERFEROMETER. The Michelson interferometer may be diagrammatically represented as shown in plate VIII, figure 13, A, B, C, and D are glass plates, A and B with faces plane and parallel; the faces M_1 and M_2 of plates D and C are optically plane and well silvered. Thus M_1 and M_2 are excellent optical plane mirrors. It is common to half silver the surface of M of plate A, but is not absolutely necessary.

Let a represent a single ray from a broad source, which on striking the surface M is partly reflected as ray 1, and partly transmitted as ray 2. On striking mirror M_1, ray 1 is reflec-

ted as ray 1' which finally falls on the eye at point E. Ray 2 after traversing plate B and after reflection at mirror M_2, retraces its path as ray 2', and finally after reflection at M, travels to the eye at point E. Since rays 1' and 2' originally came from the same source, we have conditions suitable for interference. When a broad source of light is used in the whole field of view, fringes are seen.

USE AND THEORY OF INSTRUMENT. In order to adjust and use the instrument, the plane mirror M_2 can be altered by adjusting screws, while mirror M_1 can be moved parallel to itself over some distance. Plate B, equal in thickness to plate A, is inserted between M and M_2 for the purpose of making the optical paths of the two interfering beams similar.

Now, if the instrument has been adjusted to give good fringes with an approximately monochromatic source, a sodium flame for example, a reading of the slow motion screw at M_1 can be taken. Then by slow motion of the screw, M_1 is moved a small distance d cm., which increases the optical path of ray 1 2d cm.

During the time that the path difference is increased by one wave-length, at any given place a bright fringe changes to dark and back again to bright (a shift of one fringe) it follows that the slow motion of M_1 will cause a continuous shift of fringes. If the change of bright to bright takes place n times when the mirror M is moved d cm., distance, then

$$N\lambda = 2d$$

Therefore, by means of a micrometer screw the distance d cm. can be measured which enables us to evaluate accurately the wave-length of λ.

Conversely, if the source emitting a known wave-length is used, the same relationship provides us with an exact means of measuring small distances.

THE FABRY AND PEROT ETALON. The Fabry and Perot etalon consists essentially of two glass plates, the inner surfaces of which, AB, CD, in plate VIII, figure 14, are optically plane, accurately parallel, "half" silvered, and separated by a layer of air. If approximately parallel light is incident on this arrangement, then, due to the multiple reflections and transmissions, many emergent parallel bundles of rays are present. In the figure only one bundle is shown. Since there is an infinite number of parallel bundles, all of which make the same angle with the normal to the silvered surfaces, if p is a maximum (bright fringe), it follows that all points on the circle passing through P with F as center, are also bright. In other words, we have a series of bright circular fringes formed. The maxima are narrower as one proceeds outward. The reason for this is found in the fact that there are several interfering beams.

USE OF THE INSTRUMENT. By means of the Fabry and Perot etalon in which the path difference is great and the fringes

PLATE IX

Lummer-Gehrcke Plate

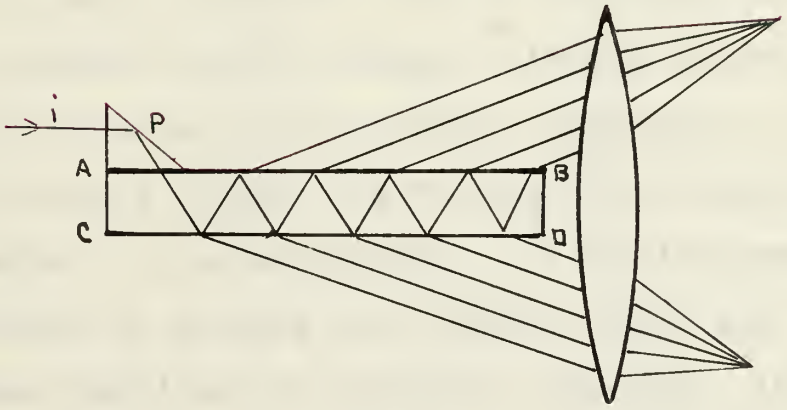

Figure 15

Lummer-Gehrcke Fringes

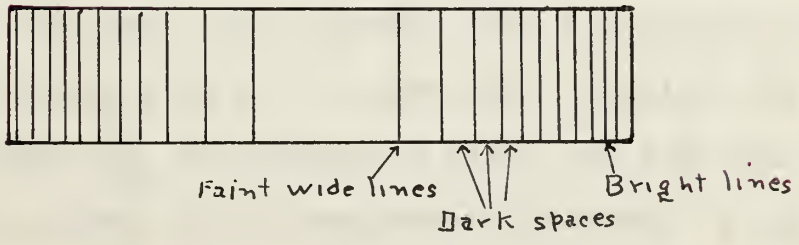

Figure 16

sharp and narrow, analysis of a single spectral line can be obtained. The distance between the two silvered plates can be changed to many centimeters and the necessary large path for such an analysis can be obtained. Another important use of this interferometer is the accurate comparison of wave-lengths. This is possible because the value of the radius of any fringe is a function of the wave-length. If now two wave-lengths from a source or sources are utilized, there are two systems of rings whose radii may be accurately measured. If one of these wave-lengths is known to a high degree of accuracy, then the wave-length of the other may be found to the same degree of accuracy by using a simple relation involving radii of corresponding rings.

THE LUMMER-GEHRCKE PLATE. Parallel bundles of interfering rays may be obtained by means of a comparatively simple device called a Lummer-Gehrcke plate. The essential part of the instrument is just a long narrow glass (or quartz) plate, and its effectiveness lies in the fact that the sides AB and CD, in plate IX, figure 15, are optically plane and parallel. A small reflecting prism, P, is cemented at one end. A ray, i, is introduced through the prism into the plate, multiple reflections give rise to a bundle of parallel rays on either side of the plate, between every two of which there is the same path difference. For the same reason and with the same optical arrangement as in the Fabry and Perot etalon, interference

fringes as shown in plate IX, figure 16, are obtained. Because of the great path differences, this instrument is also much used for the analysis of a single spectral line.

SUMMARY OF FIELDS IN WHICH THE VARIOUS INSTRUMENTS ARE ESPECIALLY USEFUL

The prism spectroscope is universally used where low dispersion is required for the analysis of the spectrum. Glass prisms are usually used in the visible region; quartz, fluorite, and calcite in the ultra-violet region; and rocksalt and sylvin in the infra-red region. Objective prisms lose very little light in dispersing the rays from the stars. Prism trains give great dispersion of the light rays, but the source must be unusually bright to see the lines in the telescope. Constant deviation prisms give automatic readings of the wavelength of lines.

Diffraction grating spectroscopes give high resolution of spectral lines. Plane glass transmission gratings are used for general spectroscopic work in the visible region. Reflecting gratings, or those made generally of speculum metal, are used for general spectroscopic work in all three regions of the spectrum. The Rowland concave grating, the ace of the most important types of all gratings for the general analysis of spectra, is especially useful in the extreme ultra-violet region.

Interferometer spectroscopes have enormous resolving power and are generally used for the examination of a single line. The Michelson interferometer is used for the determination of a single spectral line and measuring small distances by the most accurate method known. The Fabry and Perot etalon

is used mainly for accurate comparisons of the wave-lengths of spectral lines. And the Lummer-Gehrcke plate,also is used in the study of the structure of individual lines.

Michelson's echelon grating has very high resolution and gives very bright spectra in the higher orders of the spectrum. It also is used to study fine structure.

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